Integrated Environmental Assessment and Management — Volume 1, Number 3—pp. 259–266

Improving Risk Assessments for Manufactured Gas Plant Soils by Measuring PAH Availability

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(Received 11 October 2004; Accepted 19 January 2005)

Original Research

ABSTRACT

Remediation of soils at oil-gas manufactured gas plant (MGP) sites is driven primarily by the human health risks posed by the carcinogenic polycyclic aromatic hydrocarbons (PAHs), particularly benzo[*a*]pyrene (BaP), that are associated with lampblack residues. Although PAHs on lampblack are tightly sorbed, risk assessments do not account for this reduced availability. A multi-investigator study of 7 oil-gas MGP site soil samples demonstrated that the dermal and ingestion absorption factors are far lower than current default assumptions used in risk assessments. Using these sample-specific absorption factors in standard risk assessment equations increased risk-based cleanup levels by a factor of 72 on average (with a range from 23 to 142 times the default level). The rapidly released fraction of the BaP in each sample, as measured by supercritical fluid extraction, was closely correlated (r^2 = 0.96) to these calculated cleanup levels. The weight of evidence developed during this research indicates that the risks posed by PAHs on lampblack are far less than assumed when using default absorption factors and that a tiered evaluation protocol employing chemical analyses, chemical release data, and in vitro bioassays can be used to establish more realistic site-specific criteria.

Keywords: Bioavailability Bioaccessibility Lampblack Ingestion Dermal absorption

INTRODUCTION

The release of hydrocarbons from contaminated soils and sediments controls the impact that these chemicals may have following contact with biological receptors (Di Toro et al. 1991). It is clear that not all the contaminants present in a given soil are equally available, and the risks may be overestimated if chemical release differences are not considered (Alexander 2000). Several studies have documented the extremely low release of polycyclic aromatic hydrocarbons (PAHs) on sooty materials such as lampblack (Bucheli and Gustafsson 2000; Stroo et al. 2000; Jonker and Koelmans 2002).

Prior work has shown that the release of hydrocarbons from such materials to aqueous media occurs in several phases. There is typically an initial phase of relatively rapid release, followed by much slower release of the less available fraction (Gustafsson et al. 1997; Berg et al. 1998; Ghosh et al. 2000). The rapidly released fraction, or F value (Loehr et al. 2003), presumably also dominates the biological uptake during relatively short-term exposures, such as during soil ingestion or dermal contact. Considerable effort has, therefore, been focused on developing rapid and inexpensive chemical assays to measure the F value for use in risk assessments.

Bioavailability is a complex phenomenon, however. The 1st step in biological uptake is the release from the environmental matrix. The limited release of contaminants from a strongly sorbing matrix such as lampblack can therefore reduce the potential for uptake. This environmental accessibility is a strong determinant of eventual bioavailability, but it is not the only factor impacting the eventual uptake of contaminants from soil. The organism exposed to contaminated soil may have complex uptake and sequestering mechanisms, and the bioavailability may differ significantly between different routes of exposure.

As a result of the complex relationship between accessibility and bioavailability, chemical measures of bioavailability need to be used with care. Organisms do exert some control over total uptake, and chemicals may even be absorbed in some cases without the need for release from the solid matrix (Landrum et al. 1992). Careful validation of chemical extraction tests designed to predict bioavailability assays is therefore essential (National Research Council 2003).

Further, accurately measuring hydrocarbon release and bioavailability and using such information in modifying risk assessments is a difficult task. A suite of tools is needed to develop a credible weight of evidence for any site-specific adjustments, and these tools should yield results that can be directly integrated into risk assessment calculations (Ehlers and Luthy 2003). Ideally, a chemical assay that directly measures the most available fraction of the total hydrocarbon concentration present in a soil could provide a valuable screening-level tool, or a Tier 1 assessment in typical risk-based evaluations (Loehr et al. 2003). In vitro assays targeting specific receptors or pathways could then be used, if needed, for more intensive higher-tier risk assessments.

In response to these needs, a multi-investigator study was initiated to evaluate PAH availability in a series of 7 soil samples from manufactured gas plant (MGP) sites in California. All these sites were impacted by PAHs on

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lampblack, a residue produced from the pyrolysis of oil to produce gas. Other residual materials were also present at oil-gas MGP sites, including tars and crude oil, but these materials are generally removed along with the concentrated lampblack deposits during cleanup, leaving behind primarily lampblack in thin seams or mixed into native or fill soils.

Lampblack is a sooty, amorphous material composed of highly aromatic carbon that tightly binds PAHs and other aromatic hydrocarbons (Hawthorne et al. 2002; Hawthorne and Miller 2003; Hong et al. 2003). Risk assessments for oil-gas MGP site soils in California are dominated by the human health risks posed by the carcinogenic PAHs (CPAH), and the exposure routes of most concern in these assessments are oral ingestion and dermal contact (California Environmental Protection Agency 1999). The 7 PAHs currently considered carcinogenic by the State of California include benzo[*a*]pyrene (B*a*P), benzo[*a*]anthracene, benzo[*b*]fluranthene, benzo[*k*]fluranthene, chrysene, dibenzo[*a*,*h*]anthracene, and indeno[1,2,3-*cd*]pyrene.

Earlier papers have reported the characteristics of the 7 lampblack samples, including the total and rapid-release PAH concentrations (Hawthorne et al. 2002), as well as the dermal bioavailability of the B*a*P in the samples (Stroo et al. 2005), the availability of PAHs in the samples to earthworms (Kreitinger et al. 2005), and the mechanisms of sorption and the partitioning behavior of the PAHs in these samples (Hong et al. 2003). In addition, in vivo and in vitro oral ingestion studies have been performed (H.-Y. Holman et al., unpublished data). Other studies included research on the leachability of hydrocarbons from lampblack and investigations of chemical fingerprinting lampblack residues. All these results are available in a final research report (RETEC 2004).

The purpose of this paper is to present an overview of these research findings and to demonstrate how the results can be incorporated into standard risk assessments to develop site-specific cleanup levels. The results also allow a unique opportunity to compare results from different availability assays on the same samples and to evaluate the ability of a chemical assay of the rapidly released fraction of the PAHs to predict the risk-based criteria developed using the results from in vitro assays.

METHODS

A total of 18 samples (OG-1–OG-18) were obtained from 7 oil-gas MGP sites in California. These samples consisted of mixtures of soil, lampblack residuals, and miscellaneous debris. Approximately 100 kg of each sample were collected. The sampling locations at each site varied with respect to the original MGP operations. For example, some samples were taken very near the locations of former gas plant equipment, such as gas holders or tar storage tanks, while other samples were composites of discrete samples that were taken from general plant process areas. In addition, 5 background samples were also taken from nonimpacted areas that were located near the MGPs. Samples were taken either from the upper 1 m of soil or from lampblack layers exposed during excavation.

Each sample was collected in the field and placed in large sealed buckets that were then transferred to the RETEC storage facility in Ithaca, New York. The samples were then screened to remove material >6.4 mm and homogenized by mixing in a rotary mixer. The amount of rejected material ranged from 0 to 30% of the total sample weight. The homogenized samples were then stored at 4°C in airtight 55-gal drums. Subsamples (approximately 5 kg each) were taken from each sample after homogenization. The subsamples were shipped overnight to each of the investigators involved in the research effort. Subsequent analyses (Hawthorne et al. 2002) have shown that the results from the distributed subsamples were comparable and that the mixing yielded highly homogeneous materials in all but 1 case.

The 7 samples selected for further detailed evaluation in separate studies were chosen to represent the range of sample variations based on the following parameters: (1) total PAH concentration and the relative fractions of light (2- and 3-ring) and heavy (4-, 5-, and 6-ring) molecular weight PAHs, (2) the total organic carbon contents, (3) the rapid- and slow-release fractions of PAHs (as determined by supercritical fluid extraction [SFE] for 20 min at 200 bar and 50°C), and (4) the particle size distributions.

Chemical availability was determined using either an aqueous rate of release (ROR) assay (Loehr and Webster 2000) or a previously developed SFE assay (Hawthorne et al. 2001). In brief, the aqueous ROR assay was performed by mixing the test soil with water and an XAD sorbent. After specific time intervals (0–120 d), the concentrations of the PAHs collected on the XAD sorbent and remaining on the soil were determined (Loehr and Webster 2000). The SFE assay was performed by flowing supercritical carbon dioxide through the soil samples and collecting the eluted PAHs at specific time intervals (0–120 min). For both ROR and SFE, the available fraction was determined by fitting a simple 2-site desorption model as previously described (Hawthorne et al. 2002).

Dermal uptake testing was performed using human cadaver skin assays (Roy et al. 1998). That method, which was used in the earlier lampblack analysis (Stroo et al. 2000), was based on measuring the flux of radiolabeled B*a*P added to the matrix of interest immediately before application. To investigate the fluxes of PAHs from MGP site samples, which had been subjected to over 60 y of weathering, the method was modified to allow direct measurement of the release of the native PAHs bound to the soil (Roy and Singh 2001).

The potential for uptake via oral ingestion was evaluated using 2 different tests: an in vitro test and an in vivo feeding study. The in vitro procedure used a simulated gastrointestinal (GI) tract system developed at Lawrence Berkeley National Lab (Holman et al. 2002). The in vivo uptake of PAHs by mice was also evaluated by careful mass balance tests in which mice were fed 4 of the lampblack samples. Details are available in the final research report (RETEC 2004). The majority of the PAHs were evidently metabolized within the mouse guts. However, phenanthrene was conserved, allowing this PAH to be used for evaluating in vivo uptake.

Risk-based cleanup levels (RBCLs) were calculated by using the in vitro dermal absorption factors (DAFs) for each sample and the in vitro ingestion absorption factors (IAFs) for B*a*P in the same samples (values given in Table 1) in standard risk assessment equations set forth in U.S. Environmental Protection Agency (USEPA) and California Environmental Protection Agency (CA EPA) risk assessment guidance documents (CA EPA 1999; USEPA 2002). These values replace the explicit DAF of 0.15 for PAHs (CA EPA 1999) and the implicit IAF of 1.0 to yield site-specific cleanup levels. For these calculations, the residential exposure scenario was assumed, other default California-specific exposure and

Table 1. Comparison of measures of availability for phenanthrene (Phen) and benzo[*a*]pyrene (B*a*P) across test samples

	ROR[a]		SFE[a]		Earthworm[b]		Dermal[c]	In vitro[d]		In vivo[e]
Sample no.	F_{BaP}	F_{Phen}	F_{BaP}	F_{Phen}	B*a*P	Phen	B*a*P	B*a*P	Phen	Phen
OG-2	0	5	15	33	17	13	0.17	0.5	1.0	0.6
OG-5	15	5	—[f]	35	1.4	0.9	0.59	1.4	15.0	0.7
OG-10	0	15	10	63	17	1.9	0.14	1.3	3.2	1.1
OG-13	NT[g]	NT	15	28	20	0.4	0.36	1.8	8.3	NT
OG-14	NT	NT	27	60	2.3	6.0	1.05	3.0	—[h]	NT
OG-17	1	12	2	42	13	8.5	0.29	0.2	0.8	NT
OG-18	8	33	22	82	—[i]	—[i]	0.25	5.0	11.1	0.6
Mean	4.8	14	15	49	12	5.1	0.41	1.9	6.6	0.75

[a] Represents fast (rapidly available) fractions expressed as a percentage. ROR = rate of release, SFE = supercritical fluid extras.
[b] Represents percentage of polycyclic aromatic hydrocarbons (PAH) absorbed by earthworm as compared to the predicted uptake based on the equilibrium partitioning model.
[c] Represents percentage of applied dose absorbed across skin section over 24 h.
[d] Represents percentage of polycyclic aromatic hydrocarbons (PAH) solubilized in simulated gastrointestinal (GI) tract.
[e] Represents percentage uptake by mice 6 h after gavage.
[f] Could not be determined: did not fit release curve criteria (apparent F very low).
[g] NT = not tested.
[h] Could not be determined: below detectable limits or chromatographic interferences too large.
[i] Bioavailability could not be determined due to 100% mortality in bioaccumulation tests.

toxicity assumptions were used, and the allowable excess cancer risk was set at 1×10^{-6}. These "risk-based cleanup levels" are provided for illustrative purposes to demonstrate the potential impact of availability measurements on risk-based criteria and are not intended to imply regulatory concurrence at this time.

The equation used for the calculation of RBCLs is

$$\mathrm{RBCL}_{\mathrm{carcinogen}} = \frac{\text{Target Risk Level}}{(\mathrm{CSF}_{\mathrm{oral}})(\mathrm{IF}_{\mathrm{oral}} + \mathrm{IF}_{\mathrm{dermal}}) + (\mathrm{CSF}_{\mathrm{inhalation}})(\mathrm{IF}_{\mathrm{inhalation}})}$$

where $\mathrm{RBCL}_{\mathrm{carcinogen}}$ is the risk-based cleanup level for carcinogenic effects (mg/kg), Target Risk Level is the target cancer risk level (unitless), IF is the intake factor (a measure of exposure in kg soil/kg body weight/d), and CSF is the cancer slope factor (the toxicity value indicating the carcinogenic potency of a chemical in mg chemical/kg body weight/d).

The equations and exposure parameters for developing the intake factors used in the RBCL equation are presented in Table 2 and are consistent with values recommended by CA EPA. As described previously, the target risk level (i.e., the allowable excess cancer risk) is set at 1×10^{-6}. The oral and inhalation CSF for B*a*P of 12 (mg/kg/d) and 3.9 (mg/kg/d), respectively, established by the CA EPA's Office of Environmental Health Hazard Assessment (CA EPA OEHHA), were used in the RBCL calculations (CA EPA 2004).

RESULTS AND DISCUSSION

The different chemical and biological assay results for each of the samples (Table 1) reveal consistent trends despite the fact that the assays were performed by different investigators, at different times, in different laboratories, and on different subsamples. In general, the PAHs in samples OG-18, OG-14, OG-10, and OG-5 had relatively high F values, while those in OG-2 and OG-17 had lower values. These results generally reflect the strength of binding (Hong et al. 2003). It should be noted that OG-5 consistently exhibited a high degree of heterogeneity and poor reproducibility of results from separate aliquots, while all the other samples appeared to be well homogenized and yielded highly reproducible results from chemical analyses of quadruplicate samples.

The results also show that the in vitro simulated gastrointestinal tract assay, which was originally developed for petroleum hydrocarbons (Holman et al. 2002), consistently overestimated the uptake of phenanthrene as measured in an in vivo uptake test (by a factor of 10 on average for the 4 samples tested by both methods). As mentioned previously, phenanthrene was the only PAH used in the in vivo uptake test because the mass recoveries of the other PAHs in the in vivo test were relatively poor, probably because of partial metabolism in the mouse guts. Nevertheless, the results suggest that the in vitro test is conservative with respect to estimating the actual uptake in vivo.

It is important to note that the in vitro test is intended as a measure of relative oral bioavailability and reflects the impact of the specific matrix on the solubilization and, therefore, availability of the PAHs for biological uptake. The use of the results from the in vitro test as an IAF in the risk assessment equation represents the bioavailability of the PAHs in the specific soil matrix relative to bioavailability in the toxicological feeding study. The implicit assumption when applying these in vitro measurements directly in the risk assessment equation, therefore, is that the bioavailability of the PAHs in the toxicological feeding study was 100%, but this work is not simply measuring the absorption previously measured in the original feeding studies used to develop cancer slope factors. It is rather an attempt to measure the environmental accessibility, that is, the release of the bound PAHs into a form that can be absorbed, but may not necessarily be absorbed in vivo.

As indicated in Table 1, the IAFs for B*a*P were higher than the *DAF*s by roughly a factor of 5 on average. However, the relative impacts of the 2 pathways on the site-specific risk-

Table 2. Intake factor equations and exposure parameters

Intake factor equations	
(1) Oral intake factor (kg/kg-d):	
$$IF_{oral} = \frac{EF_r \times ED_c \times IRS_c \times IAF \times CF}{BW_c \times AT_c} + \frac{EF_r \times ED_a \times IRS_a \times IAF \times CF}{BW_a \times AT_c}$$	
(2) Dermal intake factor (kg/kg-d):	
$$IF_{dermal} = \frac{EF_r \times ED_c \times AF \times DAF \times SA_c \times CF}{BW_c \times AT_c} + \frac{EF_r \times ED_a \times AF \times DAF \times SA_a \times CF}{BW_a \times AT_c}$$	
(3) Inhalation intake factor (kg/kg-d):	
$$InhF_{adj} = \frac{EF_r \times ED_c \times IRA_c}{BW_c \times AT_c \times PEF} + \frac{EF_r \times ED_a \times IRA_a}{BW_a \times AT_c \times PEF}$$	
Exposure parameters[a]	
AF_a	Adherence factor for soil, adult: 0.07 mg/cm^2
AF_c	Adherence factor for soil, child: 0.2 mg/cm^2
AT_c	Averaging time—carcinogens: 25,550 d
BW_a	Body weight, adult: 70 kg
BW_c	Body weight, child: 15 kg
CF	Conversion factor: 0.000001 kg/mg
DAF	Dermal absorption factor: default for PAHs 0.15 (unitless)
ED_a	Exposure duration, adult resident: 24 y
ED_c	Exposure duration, child resident: 6 y
EF_r	Exposure frequency, residential: 350 d/y
IAF	Ingestion absorption factor:[b] default 1.0 (unitless)
IRA_a	Inhalation rate, adult: 20 m^3/d
IRA_c	Inhalation rate, child: 10 m^3/d
IRS_a	Soil ingestion, adult: 100 mg/d
IRS_c	Soil ingestion, child: 200 mg/d
PEF	Particulate emission factor: 1.316×10^9 m^3/kg
SA_a	Exposed surface area for soil/dust, adult: 5,700 cm^2/d
SA_c	Exposed surface area for soil/dust, child: 2,800 cm^2/d

[a] All exposure parameters from USEPA (2002), with the exception of DAF, which is from CA EPA (1999).
[b] The oral IAF, although not always explicitly identified in the risk assessment equation, is by default assumed to be 1.0. A default IAF of 1 implies that the oral absorption of the compound evaluated in the risk assessment is assumed to be equivalent to the oral absorption of the compound inherent in the study used to develop the toxicity value (i.e., either the cancer slope factor or the reference dose).

based criteria are actually similar because the default IAF (100% relative bioavailability) is 6.7 times the default DAF of 15% absorption, which is based on studies using live rhesus monkeys (Wester et al. 1990). The lampblack IAFs are lower than those measured for native soils or soils from coal-gas MGP sites. For example, IAFs of 37 and 57% were measured for B*a*P in native clay and sandy soils, respectively (Goon 1991). The IAFs for B*a*P in soils from coal-gas MGP sites (Weyand et al. 1995) were lower than the native soil values (as low as 11%) but higher than those reported in this study. The results are to be expected because the tarry residuals found at coal-gas MGP sites sorb PAHs more tightly than native soils but less tightly than the lampblack at oil-gas MGP sites (Hawthorne et al. 2002).

Risk-based cleanup levels for B*a*P (Table 3) were calculated by using the site-specific B*a*P DAFs and IAFs as derived from the in vitro tests described previously. These values were used in the standard California risk assessment calculations for determining cleanup levels for contaminated soil under residential exposure assumptions (CA EPA 1999) in place of the default levels for B*a*P that are assumed in the California guidelines. California risk assessment guidelines specifically incorporate "default" DAF and IAF values but do not provide guidance on how to derive site-specific values and when these

Table 3. Calculated risk-based cleanup levels for individual samples

	Sample cleanup level (residential)[a]	Enhancement factor (mg BaP equiv./kg dry soil)[b]
OG-2	5.1	142
OG-5	1.6	44
OG-10	3.0	83
OG-13	1.8	50
OG-14	0.84	23
OG-17	4.8	133
OG-18	0.92	26
Mean	2.6	72
Default	0.036	1

[a] Cleanup levels calculated using 10^{-6} excess cancer risk and California risk assessment guidance, with sample-specific in vitro benzo[a]pyrene (BaP) dermal and ingestion absorption factors (Table 1) instead of default assumptions.

[b] Enhancement factor = sample-specific cleanup level divided by the default level.

site-specific values may be incorporated into risk assessments. Use of in vitro dermal uptake results directly as *DAF*s is consistent with existing guidance (USEPA 2001). Direct use of the in vitro solubilization results as *IAF*s is not yet common practice, but it is reasonable, assuming that the PAHs must first be solubilized prior to uptake.

These risk-based cleanup levels for B*a*P ranged from 0.84 to 5.1 mg/kg. Although these are not final cleanup levels and have not been either submitted to or approved by the State of California, they are the criteria that would result from using the IAFs and DAFs derived directly from the in vitro assays. The average cleanup level for all 7 samples was roughly 72 times higher than the current default cleanup level (i.e., 0.036 mg B*a*P equivalents/kg soil at a 10^{-6} excess cancer risk level).

Similar increases in risk-based criteria (ranging from 14–107 times default values) were calculated when considering only the dermal contact pathway using these in vitro dermal results to assess the risks to adults exposed to impacted soils (Stroo et al. 2004). The fact that the results from chemical release assays and both the dermal and the oral uptake in vitro assays all yield similar results provides a compelling weight-of-evidence argument that the increases in the risk-based criteria for PAHs on lampblack resulting from this research are both justified and reasonable.

The finding that the soil concentrations calculated to be protective of human health were all at least 1 order of magnitude higher than the default cleanup levels (Table 3)—and in some cases over 2 orders of magnitude higher—emphasizes the value of measuring hydrocarbon availability. Clearly, the default values considered for these risk-based calculations yield unnecessarily and unrealistically conservative values for this particular matrix and perhaps also for similar materials that tightly bind hydrophobic organics. Although this conservatism has been recognized for several years (Stroo et al. 2000), the use of chemical release and in vitro bioavailability measurements provides a quantitative method to modify the risk assessment parameters to yield more realistic but still protective cleanup levels.

The use of only the B*a*P F values and absorption factors to calculate cleanup levels for the total CPAH is justified for 3 reasons. First, the assumed carcinogenicity of B*a*P is considered to be 3 to 100 times greater than the other 6 carcinogenic PAHs, and thus the criteria for these 7 heavy (4-, 5-, and 6-ring) and nonvolatile CPAHs are typically expressed in terms of B*a*P equivalents. Second, the total concentrations of B*a*P on lampblack are greater than the concentrations of any of the other CPAHs (Stroo et al. 2000; Hawthorne et al. 2002). Finally, the F values for all of the CPAHs were similar to those measured for B*a*P (Hawthorne et al. 2002). However, situations may well exist with other materials or other regulatory environments where the use of only B*a*P may be misleading.

For each soil sample, the available B*a*P concentration was calculated by multiplying the total B*a*P concentration by the F value as determined by the SFE analyses. For each of the 6 samples for which the available B*a*P could be calculated (i.e., the samples with a measurable F value; see Table 1), the available B*a*P was closely correlated (r^2 = 0.924) to the solubilization of B*a*P during the in vitro oral uptake assay (Figure 1). In contrast, the correlation between the in vitro solubilization and total B*a*P concentration was only 0.629 (Table 4).

In fact, the correlations between the in vitro solubilization and the available concentrations were better than the correlations between solubilization and total concentrations for all 14 PAHs present at detectable levels (Table 4). Because oral ingestion is so important in the risk assessment calculations for oil-gas MGP site soils, these results suggest that the rapidly released fraction may largely determine the actual risk and that measurements of the F values can provide useful predictions of the eventual site-specific cleanup levels.

The predictive value of chemical availability assays was evaluated by comparing the calculated site-specific cleanup levels with the rapidly released fractions (F values) of the total B*a*P as determined by SFE (Figure 2). Only 6 of the samples could be used in this comparison because the F value for OG-5 could not be measured. The results demonstrate that a close correlation (r^2 = 0.96) exists between the F values and the cleanup levels, even though the dermal uptake, oral uptake, and SFE analyses were performed by 3 separate

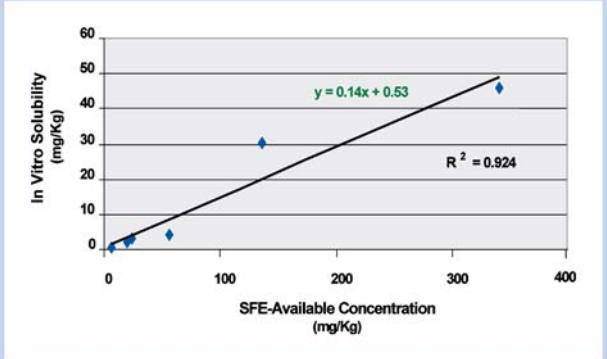

Figure 1. Relationship between the amounts of benzo[*a*]pyrene solubilized during the in vitro simulated gastrointestinal tract assay and the total amounts of "available" benzo[*a*]pyrene (total concentration multiplied by the F value).

Table 4. Correlations of in vitro uptake to total and SFE-derived available concentrations

	r^2 Values	
PAH[a] compound	Available	Total
Naphthalene	0.939	0.866
Acenaphthene	0.891	0.354
Fluorene	0.984	0.747
Phenanthrene	0.647	0.434
Anthracene	0.870	0.529
Fluoranthene	0.728	0.678
Pyrene	0.760	0.707
Benz[*a*]anthracene	0.786	0.435
Chrysene	0.900	0.626
Benzo[*b,k*]fluorene	0.986	0.454
Benzo[*a*]pyrene	0.924	0.629
Dibenz[*a,h*]anthracene	0.680	0.007
Benzo[*ghi*]perylene	0.884	0.442
Indeno[1,2,3-*cd*]pyrene	0.883	0.348

[a] PAH = polycyclic aromatic hydrocarbon.

research groups, using separate subsamples of the same homogenized initial site samples. Over the range of availabilities measured, the best-fit linear relationship (not shown) was $y = 5.23 - 0.18x$, which also provided a close correlation ($r^2 = 0.89$).

The total B*a*P concentrations in the samples had no relationship to the calculated cleanup levels (r^2 values of only 0.19 and 0.26 for the best-fit linear and exponential relationships, respectively). Similarly, the relative abundance the other CPAH compounds did not exhibit significant correlations with the calculated cleanup levels.

These results suggest that the strong sorption of PAHs to the lampblack matrix has a large effect on the ability of organisms to absorb the PAHs as well as on the availability of the PAHs for release under the relatively mild extraction conditions used in the SFE or ROR analysis. Further, the F values and the individual bioavailability results were closely correlated, suggesting that biological uptake in fact occurs primarily from the fraction of the total concentration that is available for rapid desorption.

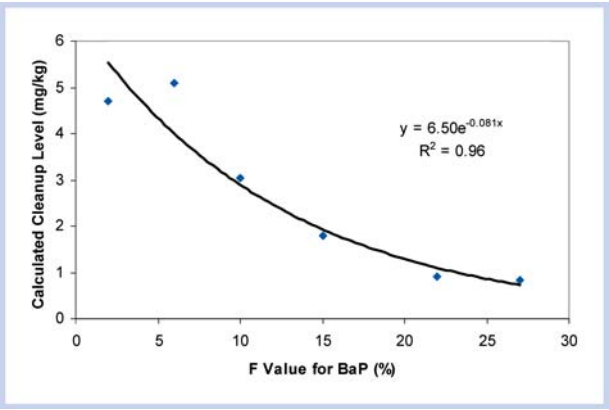

Figure 2. Relationship between the risk-based cleanup levels for carcinogenic polycyclic aromatic hydrocarbon (PAH), expressed as benzo[*a*]pyrene (B*a*P) equivalents and calculated using the sample-specific dermal and ingestion absorption factor and the percentage of B*a*P in the fast-release fraction (F value) for each sample as determined by supercritical fluid extraction.

Related work on these samples indicates that there are essentially 2 pools of PAHs on lampblack: PAHs bound directly to the lampblack matrix and PAHs present as a separate phase that cannot bind directly to the lampblack because the surface area available for direct binding is saturated (Hong et al. 2003). For example, the sample with the highest PAH:total organic carbon (TOC) ratio (and therefore presumably the largest fractions of "free-phase" PAHs) also had the highest F value and the lowest calculated cleanup level (i.e., OG-18). Consistent with this hypothesis, OG-2 had the lowest PAH:TOC ratio and also a low F value and the highest cleanup level.

The interrelated research done on this set of oil-gas MGP site samples represents the 1st such integrated study of chemical release and bioavailability on a common solid matrix. The results support the overall hypothesis of this work, which is that the risks of hydrocarbons to human health are strongly affected by the strength with which the hydrocarbons are bound to the solid matrix and that the risks can be more reasonably predicted by chemical release and bioavailability assays. The weight of evidence developed by this multi-investigator research effort indicates that the risks posed by PAHs on lampblack are far less than assumed when using default absorption factors and that a tiered evaluation protocol employing chemical assays, chemical release data (F values), and in vitro assays can be used to establish more realistic site-specific criteria.

In this case, a simple 40-min SFE test under defined conditions provided an exceptional correlation to the risk-based cleanup levels derived from much more costly and time consuming in vitro bioavailability assays. That relationship spans a range of rapidly released fractions from 2 to 27%, using a series of samples of lampblack-impacted soils from several oil-gas MGP sites in California.

These results are not necessarily limited to the human health risks of PAHs on lampblack or to the use of SFE as an analytical method. Prior work with these and other samples has shown that the rapidly released fractions measured by SFE extraction are closely correlated to those measured by the aqueous ROR assay (Hawthorne et al. 2002). Further, rates of release have been measured for a wide range of hydrocarbons in 40 different field samples, leading to a calibrated 7-d batch desorption test that accurately estimates sample-specific F values without the need for SFE equipment or expertise (Loehr et al. 2003). Finally, the F values as determined by SFE for these oil-gas MGP site samples and a similar set of samples from coal-gas MGP sites have been shown to correlate closely to the uptake of PAHs by earthworms (Kreitinger et al. 2005). These results indicate that chemical availability assays may also be useful in evaluating ecological risks.

In a practical sense, the proposed approach to developing risk-based criteria requires careful measurement of the B*a*P release and/or in vitro absorption measurements. Given the importance of B*a*P in setting criteria for oil-gas MGP site residuals, this approach is justified, but rigorous QA/QC and

use of multiple replicates and site samples will probably be needed to reduce the inherent uncertainty.

Additionally, this work has deliberately used samples containing relatively high PAH concentrations because of the relatively high detection limits for PAHs by conventional analytical methods, which are particularly problematic when attempting to measure release or uptake from materials that sorb hydrocarbon so tightly. Analytical refinements will be needed to ensure reliable measurements of the rapidly released fractions from lower-concentration soil samples that are closer to the estimated risk-based criteria. The approach used in this work is predicated on the assumption that the PAHs in the lower-concentration samples are associated with lampblack particles but that these particles are simply more dispersed throughout the soil matrix. Evidence from examinations of these samples indicates that this assumption is valid because virtually all the PAHs were found on the lampblack particles and not on the separated "soil" fraction (Hong et al. 2003).

CONCLUSIONS

This integrated study of 7 oil-gas MGP site samples included a series of chemical and biological assays designed to develop a weight-of-evidence approach for measuring contaminant bioavailability that is consistent with the guidance developed by the National Research Council Committee on Bioavailability (2003). Several investigators using different assays have all shown that the availability of PAHs on lampblack is far lower than is assumed in the standard risk assessment guidance used in California (California EPA 1999) or by the USEPA (1991). Further, a protocol based on the use of in vitro assays for both dermal and oral ingestion of B*a*P (by far the most important PAH in determining risk-based criteria for oil-gas MGP site soils) yielded calculated risk-based cleanup criteria that are 23 to 142 times higher than the default criteria (72 times higher on average).

Finally, the F values for B*a*P in these oil-gas MGP site samples has been demonstrated to be closely correlated to the in vitro results. This relationship suggests that most of the biological uptake of B*a*P occurs from the fraction that is available for rapid release. The SFE, under conditions previously developed to measure the rapidly released fraction of the total PAH concentration in a soil sample (Hawthorne et al. 2001), provided an exceptionally accurate prediction of the uptake during the in vitro tests and therefore of the calculated risk-based criteria. The SFE, or the closely correlated batch desorption method to estimate F values (Loehr et al. 2003), can therefore provide rapid and inexpensive screening-level assessments of the chemical release, bioavailability, and associated risks of PAHs in a particular oil-gas MGP site sample.

Acknowledgement—This work was funded by the Gas Technology Institute, the Southern California Gas Company, Southern California Edison, and Pacific Gas & Electric. The advice and guidance of Ron Jensen, Anita Bohrnerud, Robert Doss, Dianne Saber, and Steve DiZio are deeply appreciated. SBH also acknowledges the partial financial support of the U.S. Department of Energy under Cooperative Agreement DE-FC26-98FT40321. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE or any of the funding organizations.

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